

**TITLE: FUNCTIONALIZED POLYMER COMPOSITION FOR GREASE**

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**FIELD OF THE INVENTION**

The present invention relates to a grease in particular a lubricating grease comprising: (a) an esterified polymer derived from monomers comprising: (i) a vinyl aromatic monomer; (ii) an unsaturated dicarboxylic acid anhydride or derivatives thereof; (b) a thickening agent; and (c) an oil of lubricating viscosity, wherein the esterified polymer contains titratable acid groups. The invention further relates to the process to make the composition and its use.

**BACKGROUND OF THE INVENTION**

It is known to prepare greases from base oil, a thickener and optionally other performance additives for example antioxidants or antiwear agents. Polymers have also been added to greases in an attempt to improve the performance characteristics of the grease, for example, polymers have been employed to decrease water wash-off, to increase water repellency, to decrease oil separation, to increase dropping points or cone penetration and as thickeners. Often the polymers of polymethacrylates or polyolefins are added to grease. Typically these polymers are incorporated in the base oil and act as a viscosity modifier. However, the polymers have limited interaction with the thickener. This results in the grease being more susceptible to the effects of water, for example, water wash-off or decreased water repellency. Producing greases with poor water wash-off or water repellency decreases the longevity of grease and increases wear on the surface being lubricated.

Japanese Patent Application 04-046997 A2 (Tanaka et al, Showa Shell) discloses a hydrolysed or un-hydrolysed maleic anhydride-styrene-oxyalkylene copolymer capable of imparting water resistance to greases. The oxyalkylene monomer is required to impart oil solubility.

US Patent Number 5,858,934 (Wiggins et al., Lubrizol Corporation) discloses a pour point depressing amount of an interpolymer maleic anhydride-styrene copolymer suitable for use in biodegradable vegetable oil greases. The



(4) adding the solvated polymer containing an ester or derivatives thereof of step (2) or the amidated polymer of step (3) to a thickening agent, an oil of lubricating viscosity or mixtures thereof; and

5 (5) optionally adding to the product of step (4) adding at least one other performance additive to form a grease composition.

The present invention further provides a grease composition containing polymers capable of improving greases by imparting improved water wash-off and water repellence. The invention further provides a grease composition containing polymers capable of improving thickening. The invention further provides a grease composition containing polymers capable of decreasing wear and increasing longevity.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a grease composition comprising:

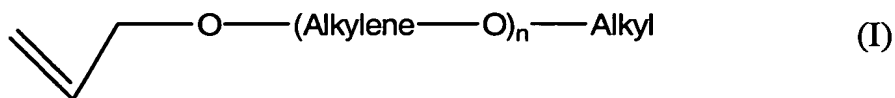
- 15 (a) an esterified polymer derived from monomers comprising:
- (i) a vinyl aromatic monomer;
  - (ii) an unsaturated dicarboxylic acid anhydride or derivatives thereof;
- (b) a thickening agent; and
- (c) an oil of lubricating viscosity,

20 wherein the esterified polymer contains titratable acid groups with a total acid number of at least about 4.

The titratable acid groups located on the carbon atoms of the esterified polymer are adjacent to each other, randomly dispersed or mixtures thereof. The level of titratable acid groups as measured by titration and expressed as mg KOH/gram of sample may be expressed as a Total Acid Number (TAN) in the range

25 from about 4 to about 150, preferably about 5 to about 100, more preferably about 8 to about 80, even more preferably about 8 to about 60 and most preferably about 8 to 50 per mole.

In one embodiment the polymer is free of units derived from an oxyalkylene monomer including those represented by the formula:



wherein the alkylene includes  $-\text{CH}_2-$ ,  $-\text{C}_2\text{H}_4-$ ,  $-\text{C}_3\text{H}_6-$ ,  $\text{C}_4\text{H}_8-$  or mixtures thereof; n is a repeat unit that may be present from 1 to about 60 times; and the alkyl group may contain 1 to about 20 carbon atoms.

The molecular weight of the polymer derived from component (a) monomers  
5 (i) a vinyl aromatic monomer and (ii) an unsaturated dicarboxylic acid anhydride or derivatives thereof, is controlled using a variety of known techniques such as reaction temperature, initiators, monomer concentration and chain transfer agents. The molecular weight ( $M_n$ ) of the polymer is in the range from about 20,000 to about 500,000, preferably about 24,000 to about 400,000, more preferably about  
10 28,000 to about 350,000, and most preferably about 32,000 to about 300,000.

The molecular weight of the copolymer (also referred to as an interpolymer) of a vinyl aromatic monomer and an unsaturated dicarboxylic acid anhydride or derivatives thereof from which component (a) of the invention is made may also be expressed in terms of the "reduced specific viscosity" of the polymer which is a  
15 widely recognized means of expressing the molecular size of a polymeric substance. As used herein, the reduced specific viscosity (abbreviated as RSV) is the value obtained in accordance with the formula  $\text{RSV} = (\text{Relative Viscosity} - 1)/\text{Concentration}$ , wherein the relative viscosity is determined by measuring, by means of a dilution viscometer, the viscosity of a solution of about 1g of the  
20 polymer in about  $10\text{ cm}^3$  of acetone and the viscosity of acetone at about  $30^\circ\text{C}$ . For purpose of computation by the above formula, the concentration is adjusted to about 0.4g of the interpolymer per  $10\text{ cm}^3$  of acetone. A more detailed discussion of the reduced specific viscosity, also known as the specific viscosity, as well as its relationship to the average molecular weight of an interpolymer, appears in Paul J.  
25 Flory, Principles of Polymer Chemistry, (1953 Edition) pages 308 et seq. The interpolymer polymer has a RSV from about 0.05 to about 2 preferably about 0.1 to about 1 and most preferably about 0.1 to about 0.8. In one embodiment the RSV is about 0.69.

When incorporated into the interpolymer from which the esterified polymer  
30 is made the unsaturated dicarboxylic acid anhydride or derivatives thereof loses unsaturated functionality to become the dicarboxylic acid anhydride or derivatives thereof. The dicarboxylic acid anhydride or derivatives thereof is present in the

esterified polymer from about 0.1 to about 1, preferably about 0.7 to about 1, more preferably about 0.8 to about 1, even more preferably about 0.95 to about 1 and most preferably about 1 to about 1 mole equivalents relative to the amount of the vinyl aromatic monomer.

- 5           The esterified polymer is present in a grease composition from about 0.01 to about 30, preferably about 0.04 to about 20, even more preferably about 0.06 to about 10 and most preferably about 0.08 to about 5 weight percent of the grease composition. The esterified polymer may be used alone or in combination.

#### Vinyl Aromatic Monomer

- 10           The esterified polymer contains a vinyl aromatic monomer. Suitable examples of a vinyl aromatic monomer include styrene (often referred to as ethenylbenzene), substituted styrene or mixtures thereof. Substituted styrene monomers include functional groups such as a hydrocarbyl group, halo-, amino-, alkoxy-, carboxy-, hydroxy-, sulphonyl- or mixtures thereof. The functional groups  
15 are located at the ortho, meta or para positions relative to the vinyl group on the aromatic monomer, although preferably the functional groups are located at the ortho or para position; and most preferably at the para position. Halo- functional groups include chlorine, bromine, iodine or mixtures thereof. Preferably the halo functional group is chlorine or mixtures thereof. Alkoxy functional groups can  
20 contain 1 to about 10, preferably 1 to about 8, more preferably 1 to about 6 and most preferably 1 to about 4 carbon atoms. Alkoxy functional groups containing 1 to about 4 carbon atoms is referred to as lower alkoxy styrene.

- The hydrocarbyl group includes alkyl, alkoxy, cycloalkyl, acyclic, aryl or mixtures thereof; and the functional groups can be branched or linear. The  
25 hydrocarbyl group contains 1 to about 30, preferably 1 to about 20, more preferably 1 to about 15 and most preferably 1 to about 10 carbon atoms. Examples of a suitable hydrocarbyl group on styrene monomers include alpha-methylstyrene, para-methylstyrene (often referred to as vinyl toluene), para-tert-butylstyrene, alpha-ethylstyrene, para-lower alkoxy styrene or mixtures thereof.

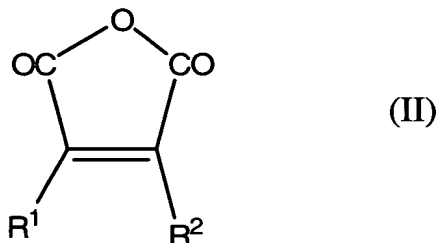
- 30           Examples of para-lower alkoxy styrene include para-methoxy styrene, para-ethoxy styrene, para-propoxy styrene, para-butoxy styrene or mixtures thereof. Although the vinyl aromatic monomer includes styrene, a substituted styrene or

mixtures thereof, styrene is preferred. The vinyl aromatic monomer can be used alone or in combination.

The vinyl aromatic monomer is present in the esterified polymer from about 0.1 to about 1, preferably about 0.7 to about 1, more preferably about 0.8 to about 1, even more preferably about 0.95 to about 1 and most preferably about 1 to about 1 mole equivalents relative to the amount of the dicarboxylic acid anhydride or derivatives thereof.

#### Unsaturated Dicarboxylic acid Anhydride or Derivatives Thereof

The esterified polymer further contains at least one monomer derived from and unsaturated dicarboxylic acid anhydride or derivatives thereof. The unsaturated dicarboxylic acid anhydride or derivatives thereof include those derived from a maleic anhydride represented by the formula:



wherein  $R^1$  and  $R^2$  are independently hydrogen or a hydrocarbyl group containing about 1 to about 40, preferably about 1 to about 30, more preferably about 1 to about 20 and most preferably about 1 to about 10 carbon atoms. The carbon atoms of the hydrocarbyl group include alkyl, alkylaryl, cycloalkyl, aryl or mixtures thereof. The hydrocarbyl group includes substituted, unsubstituted, branched, unbranched or mixtures thereof, although, unsubstituted is preferred.

The unsaturated dicarboxylic acid anhydride or derivatives thereof may be wholly or partially esterified. When partially esterified other derivatives include acids, salts or mixtures thereof.

Suitable salts include alkali metals, alkaline metal or mixtures thereof. The salts include lithium, sodium, potassium, magnesium, calcium or mixtures thereof.

Suitable examples of the unsaturated dicarboxylic acid anhydride or derivatives thereof for the grease composition include maleic anhydride, methyl maleic anhydride, ethyl maleic anhydride, dimethyl maleic anhydride or mixtures

thereof. The unsaturated dicarboxylic acid anhydride or derivatives thereof functionality can be used alone or in combination.

#### Alkyl Acrylate or Alkyl Methacrylate Monomer

Optionally, the esterified polymer described above contains an alkyl acrylate or alkyl methacrylate monomer. The alkyl group of the acrylate or methacrylate contains 1 to about 20, preferably 1 to about 10, more preferably 1 to about 5 and most preferably 1 to about 2 carbon atoms. The alkyl acrylate or alkyl methacrylate monomer is present from 0 to about 15 mole %, about 1 to about 10 mole %, and most preferably about 2 to about 8% relative to the amount of vinyl aromatic monomer.

Examples of a suitable alkyl acrylate or alkyl methacrylate monomer include methyl acrylate, ethyl acrylate, propyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate or mixtures thereof. In one embodiment the alkyl acrylate is methyl acrylate and in another embodiment the alkyl methacrylate is methyl methacrylate. The alkyl acrylate or alkyl methacrylate monomer may be used alone or in combination.

#### Alcohols

The esterified polymer is formed by reaction of the dicarboxylic acid anhydride or derivatives thereof with an alcohol to form esterified groups. The alcohol reacts with a portion of the dicarboxylic acid anhydride or derivatives thereof thus forming an ester, a half-ester or mixtures thereof and unsaturated bonds are partially or wholly saturated. The portion of the partially or wholly saturated dicarboxylic acid anhydride or derivatives thereof that do not react with alcohol remain titratable.

The conversion of dicarboxylic acid anhydride or derivatives thereof to ester groups include those in the range of about 50 % to about 99.5 %, preferably about 80 % to about 99.5 %, more preferably about 84 % to about 99.5%, even more preferably about 88% to about 99.5 % and most preferably about 92 % to about 99 %.

The alcohols suitable for the invention include those with about 6 to about 24, preferably about 6 to about 20, more preferably about 8 to about 20 and most preferably about 8 to about 18 carbon atoms. The carbon atoms of the alcohol

include a hydrocarbyl group, preferably, alkyl or cycloalkyl, more preferably alkyl or mixtures thereof. The alcohol is may be linear, branched or mixtures thereof, although preferably branched. The branched alcohols are present in an amount greater than about 5, preferably greater than about 10, more preferably greater than  
5 about 20, even more preferably greater than about 40 and most preferably greater than about 60 wt % of the alcohol molecules present.

In one embodiment the alcohol is a mixture containing at least one alcohol with about 6 to about 11, preferably about 6 to about 10 and most preferably about 8 to about 10 carbon atoms; and at least one alcohol with about 12 to about 24,  
10 preferably about 12 to about 20 and most preferably about 12 to about 18 carbon atoms. The weight percentage ratio of an alcohol containing about 6 to about 11 to an alcohol containing about 12 to about 24 is in the range of about 99:1 to about 1:99, preferably about 50:50 to about 10:90, more preferably about 40:60 to about 15:85, even more preferably about 35:65 to about 15:85 and most preferably about  
15 20:80 to about 30:70. In one embodiment the weight percentage ratio of an alcohol containing about 6 to about 11 to an alcohol containing about 12 to about 24 is about 25:75.

Suitable examples of alcohols include hexanol, heptanol, octanol, isooctanol, 2-ethylhexanol, nonanol, decanol, isodecanol, dodecanol, tridecanol, butadecanol,  
20 myristol, pentadecanol, palmitol, hexadecanol, heptadecanol, stearyl, octadecanol, icosyldecanol, icosanol, decan-2-ol, isodecan-2-ol, dodecan-2-ol, tridecan-2-ol, butadecan-2-ol, pentadecan-2-ol, hexadecan-2-ol, heptadecan-2-ol, octadecan-2-ol, icosyldecan-2-ol, icosan-2-ol, decan-3-ol, isodecan-3-ol, dodecan-3-ol, tridecan-3-ol, butadecan-3-ol, pentadecan-3-ol, hexadecan-3-ol, heptadecan-3-ol, octadecan-3-ol,  
25 ol, icosyldecan-3-ol, icosan-3-ol, isononanol, isodecanol, isododecan-2-ol, isotridecan-2-ol, isobutadecan-2-ol, isopentadecan-2-ol, isohexadecan-2-ol, isoheptadecan-2-ol, isooctadecan-2-ol or mixtures thereof. Preferably the alcohols include octanol, isooctanol, 2-ethylhexanol, nonanol, decanol, dodecan-2-ol, tridecan-2-ol, butadecan-2-ol, pentadecan-2-ol, hexadecan-2-ol, heptadecan-2-ol,  
30 octadecan-2-ol, isononanol, isodecanol, isododecan-2-ol, isotridecan-2-ol, isobutadecan-2-ol, isopentadecan-2-ol, isohexadecan-2-ol, isoheptadecan-2-ol, isooctadecan-2-ol or mixtures thereof. When mixtures of alcohols are used in the



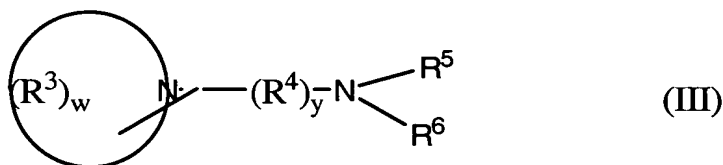
invention, the alcohols are available as mixtures for example Alfol C8C10® Alcohols or Alfol C12C18® Alcohols and the like.

In one embodiment alcohol with less than about 6 carbon atoms is used in combination with an alcohol containing about 6 to about 24 carbon atoms. Suitable  
5 examples include propanol, butanol, pentanol or mixtures thereof. In one embodiment the alcohol with less than about 6 carbon atoms is butanol.

#### Amine

The esterified polymer optionally contains at least one amine includes a monoamine, a polyamine or mixtures thereof. The amine contains primary  
10 functionality, secondary functionality or mixtures thereof. The amine includes cyclic, linear or branched and include an alkylenemonoamine, a heterocyclic monoamine, an alkylenepolyamine, a heterocyclic polyamine or mixtures thereof, preferably the amine contains not more than one primary or secondary amino group, for example N,N-dimethylaminopropylamine.

15 In one embodiment the amine compounds are represented by the formula:



wherein  $R^3$  includes atoms bonded to form mono- or poly- nuclear rings; and the atoms include carbon, oxygen, nitrogen, phosphorus or mixtures thereof.  
20 Preferably  $R^3$  includes carbon, oxygen, nitrogen or mixtures thereof.

The mononuclear cyclic structure contains about 5 to about 8 atoms and preferably about 6 to about 7 atoms. The polynuclear cyclic structure contains about 8 to about 16 and preferably about 10 to about 12 atoms.  $w$  is in the range from about 4 to about 15, preferably about 5 to about 11, more preferably  
25 about 5 to about 8 atoms. The cyclic ring includes aromatic, non-aromatic or mixtures thereof, although non-aromatic is preferred.

$R^4$  includes alkyl or alkenyl group with  $y$  containing about 1 to about 8, preferably about 1 to about 6, and most preferably about 2 to about 5 carbon atoms. The alkyl or alkenyl group include substituted, unsubstituted, branched,

unbranched alkylaryl, cycloalkyl or mixtures thereof. Suitable examples of R<sup>4</sup> include ethyl, propyl, butyl, pentyl or mixtures thereof. Preferably R<sup>4</sup> is ethyl, propyl or mixtures thereof.

R<sup>5</sup> and R<sup>6</sup> are independently hydrogen or a hydrocarbyl group, preferably at least one, and most preferably both of R<sup>5</sup> and R<sup>6</sup> are hydrogen. When R<sup>5</sup> or R<sup>6</sup> is a hydrocarbyl group, the number of carbon atoms present is in the range from about 1 to about 8, preferably about 1 to about 5 and most preferably about 1 to about 3 or mixtures thereof. Suitable examples of a hydrocarbyl group include methyl, ethyl, propyl, butyl, pentyl or mixtures thereof.

Examples of suitable cyclic amines include 4-(3-aminopropyl) morpholine, 4-(3-aminoethyl) morpholine or mixtures thereof. Preferably the cyclic amine is 4-(3-aminopropyl) morpholine and may be used alone or in combination.

The amines when present are in an effective amount to substantially react with the unsaturated dicarboxylic acid anhydride or derivatives thereof and leaving no residual amine present in the esterified polymer. Typically the amine is present weight percent based on the total weight of the polymer in the range from about 0 to about 1, preferably about 0.1 to about 1, more preferably about 0.2 to about 1 and most preferably about 0.4 to about 1 equivalents of the unsaturated dicarboxylic acid anhydride or derivatives thereof.

In one embodiment the polymer described above does not contain Mannich base functionality. The Mannich base is formed by the reaction of (a) an aldehyde, with (b) a phenols and (c) at least one non-monomeric amine with primary functionality, secondary functionality or mixtures thereof.

#### The Thickening Agent

Thickening agents such as metal salts of carboxylic acids are known in the art of grease formulation. The metal is an alkali metal, alkaline earth metal, aluminium or mixtures thereof. Examples of suitable metals include lithium, potassium, sodium, calcium, magnesium, barium, aluminium or mixtures thereof. Preferably the metal is lithium, calcium, aluminium or mixtures thereof.

The carboxylic acid used in the thickener is a fatty acid and a mono-hydroxycarboxylic acid, a di-hydroxycarboxylic acid, a poly-hydroxycarboxylic acid

or mixtures thereof. The carboxylic acid has about 4 to about 30, preferably about 8 to about 27, more preferably about 19 to about 24 and most preferably about 10 to about 20 carbon atoms and includes derivatives thereof such as an ester, a half ester, salts, anhydrides or mixtures thereof. Examples of suitable fatty acids include capric acid, palmitic acid, stearic acid, oleic acid or mixtures thereof. Preferably the fatty acid is a stearic acid.

In one embodiment the carboxylic acid thickener is a di-hydroxycarboxylic acid, a poly-hydroxycarboxylic acid or mixtures thereof. Alternatively the di-carboxylic acid include iso-octanedioic acid, octanedioic acid, nonanedioic acid (azelaic acid), decanedioic acid (sebacic acid), undecanedioic acid, dodecanedioic acid, tridecanedioic acid, tetradecanedioic acid, pentadecanoic acid or mixtures thereof. The di-carboxylic acid and poly-carboxylic acid tend to be more expensive than mono-carboxylic acid and as a consequence, most industrial processes using mixtures preferably use a weight ratio of dicarboxylic and/or polycarboxylic acid to monocarboxylic acid in the range about 15:85 to about 40:60, more desirably about 20:80 to about 35:65, and more preferably about 25:75 to about 35:65. Many commercial manufacturers use a blend of about 30:70.

In one embodiment the carboxylic acid thickener is a hydroxy-substituted fatty acid or mixtures thereof. A particularly preferred hydroxy-substituted fatty acid is hydroxy stearic acid. Suitable examples include 10-hydroxystearic acid, 12-hydroxystearic acid, 14-hydroxystearic acid or mixtures thereof. In one embodiment the hydroxy-substituted fatty acid is 12-hydroxystearic acid.

The thickener can also be prepared directly from at least one fatty acid source, such as vegetable oil or animal fats, by saponification. The thickener is prepared directly from a fatty acid including hydrogenated castor oil, glyceride or other esters containing alkyl groups. The alkyl groups contains about 1 to about 10, preferably about 1 to about 5 and most preferably about 1 to about 3 carbon atoms. Suitable examples of alkyl groups for the fatty acid esters include methyl, ethyl, propyl, butyl, pentyl, glycerol or mixtures thereof.

In one embodiment thickening agents include inorganic powders include clay, organo-clays, bentonite, fumed silica, calcite, carbon black, pigments, copper

phthalocyanine or mixtures thereof. In one embodiment the calcite containing thickeners made from overbased calcium sulphonate or carboxylates are used.

The thickener is present in the range from about 3 to about 40, preferably from about 4 to about 35, even more preferably about 4 to about 30, even more preferably about 5 to about 25 and most preferably from about 5 to about 20 weight percent of the grease composition. The thickener may be used alone or in combination.

#### Oil of Lubricating Viscosity

The grease composition includes natural or synthetic oils of lubricating viscosity, oil derived from hydrocracking, hydrogenation, hydrofinishing, unrefined, refined and re-refined oils or mixtures thereof.

Natural oils include animal oils, vegetable oils, mineral oils or mixtures thereof. Synthetic oils include a hydrocarbon oil, a silicon-based oil, a liquid esters of phosphorus-containing acid. Synthetic oils include those produced by Fischer-Tropsch reactions and hydroisomerised Fischer-Tropsch hydrocarbons or waxes.

Oils of lubricating viscosity is defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. In one embodiment the oil of lubricating viscosity comprises an API Group I, II, III, IV, V or mixtures thereof, and preferably API Group I, II, III or mixtures thereof. If the oil of lubricating viscosity is an API Group II, III, IV or V oil there up to about 40 wt % and most preferably up to a maximum of about 5 wt % of the lubricating oil an API Group I oil.

The oil of lubricating viscosity is present from about 20 to about 97, preferably from about 40 to about 96, even more preferably about 60 to about 96 and most preferably from about 67 to about 95 weight percent of the grease composition. The oil of lubricating viscosity may be used alone or in combination.

#### Other Performance Additives

Optionally, the grease composition includes at least one other performance additives which include antioxidants, rust inhibitors, metal deactivators, antiwear agents, antiscuffing agents, extreme pressure agents, foam inhibitors, demulsifiers, friction modifiers, viscosity modifiers, pour point depressants or mixtures thereof.

The other performance additives are present in the range from 0 to about 20, preferably about 0.1 to about 15, even more preferably about 0.2 to about 10 and most preferably about 0.4 to about 10 weight percent of the grease composition. In one embodiment one or more of the other performance additives  
5 are present and it is common for the performance additives to be present in different amounts relative to each other.

#### Antioxidants

Antioxidants are known materials and include diphenylamines, sterically hindered phenols, molybdenum dithiocarbamates, sulphurised olefins and the like.  
10 The antioxidants can be used alone or in combination.

Examples of suitable diphenylamine antioxidants include octyl diphenylamine, nonyl diphenylamine, bis-octyl diphenylamine, bis-nonyl diphenylamine or mixtures thereof.

Examples of sterically hindered phenols include 2,6-di-tert-butylphenol, 4-  
15 Methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol, 4-butyl-2,6-di-tert-butylphenol, 2,6-di-tert-butylphenol, 4-pentyl-2,6-di-tert-butylphenol, 4-hexyl-2,6-di-tert-butylphenol, 4-heptyl-2,6-di-tert-butylphenol, 4-(2-ethylhexyl)-2,6-di-tert-butylphenol, 4-octyl-2,6-di-tert-butylphenol, 4-nonyl-2,6-di-tert-butylphenol, 4-decyl-2,6-di-tert-butylphenol, 4-undecyl-2,6-di-tert-butylphenol, 4-dodecyl-2,6-di-tert-butylphenol, 4-tridecyl-2,6-di-tert-butylphenol, 4-tetradecyl-2,6-di-tert-butylphenol, 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid butyl ester, 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid methyl ester, 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid 2-ethylhexyl ester or mixtures thereof.  
20

25 In one embodiment the sterically hindered phenol is 2,6-di-tert-butylphenol or mixtures thereof. In one embodiment the sterically hindered phenol is 4-(2-ethylhexyl)-2,6-di-tert-butylphenol or mixtures thereof. In one embodiment the sterically hindered phenol is 4-dodecyl-2,6-di-tert-butylphenol or mixtures thereof.

In one embodiment two sterically hindered phenols are linked through a  
30 bridging group typically located at position 2- or 4- relative to the hydroxyl group. The bridging group include -CH<sub>2</sub>- (methylene bridge) or -CH<sub>2</sub>OCH<sub>2</sub>- (ether bridge) or mixtures thereof. Examples of methylene-bridged sterically hindered phenols

include 4,4'-methylenebis(6-tert-butyl-o-cresol), 4,4'-methylenebis(2-tert-amyl-o-cresol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-methylene-bis(2,6-di-tertbutylphenol) or mixtures thereof.

5 Examples of suitable molybdenum dithiocarbamates include commercial materials sold under the trade names such as Vanlube 822™ and Molyvan™ A from R. T. Vanderbilt Co., Ltd., and Adeka Sakura-Lube™ S-100 and S-165 and S-600 from Asahi Denka Kogyo K. K and the like.

10 Examples of suitable sulphurised olefins include propylene, isobutylene, pentene, hexane, heptene, octane, nonene, decene, undecene, dodecene, undecyl, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof. In one embodiment, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof and their dimers, trimers and tetramers are preferred olefins. In another embodiment, the olefin is a Diels-Alder adduct of a diene such as 1,3-  
15 butadiene and an unsaturated ester such as butyl (meth) acrylate.

Sulphurised olefins include fatty acids and their esters. The fatty acids are obtained from vegetable oil, animal oil or mixtures thereof; and contains about 4 to about 22 carbon atoms. Examples of suitable fatty acids and/or their esters include triglycerides, oleic acid, linoleic acid, palmitoleic acid or mixtures thereof. The fatty  
20 acids are obtained from lard oil, tall oil, peanut oil, soybean oil, cottonseed oil, sunflower seed oil or mixtures thereof. In one embodiment fatty acids and/or their esters are mixed with alpha-olefins.

#### Antiwear Agents

25 The lubricant optionally contains an antiwear agent. Useful antiwear agents include metal thiophosphates, especially zinc dialkyldithiophosphates; phosphoric acid esters or salt thereof; phosphites; and phosphorus-containing carboxylic esters, ethers, amides and the like. The antiwear agent may be used alone or in combination.

#### Antiscuffing Agents

30 The lubricant optionally contains an antiscuffing agent. Antiscuffing agents that decrease adhesive wear include sulphur containing compounds. The sulphur containing compounds include organic sulphides and polysulphides,

such as benzyldisulphide, bis-(chlorobenzyl) disulphide, dibutyl tetrasulphide, di-tertiary butyl polysulphide, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, sulphurised Diels-Alder adducts, sulphurised fats (including vegetable oil, animal fat or mixtures thereof), sulphurised olefins, mixed co-sulphurised fats and olefins, alkyl sulphenyl N'N-dialkyl dithiocarbamates, the reaction product of polyamines with polybasic acid esters, chlorobutyl esters of 2,3-dibromopropoxyisobutyric acid, acetoxymethyl esters of dialkyl dithiocarbamic acid and acyloxyalkyl ethers of xanthogenic acids or mixtures thereof. The antiscuffing agents may be used alone or in combination.

#### Extreme Pressure Agents

Extreme Pressure (EP) agents that are soluble in the oil include sulphur and chlorosulphur-containing EP agents, chlorinated hydrocarbon EP agents, phosphorus EP agents, or mixtures thereof. Examples of such EP agents include chlorinated wax, organic sulphides and polysulphides, such as benzyldisulphide, bis-(chlorobenzyl) disulphide, dibutyl tetrasulphide, sulphurised fats (including vegetable oil, animal fat or mixtures thereof), sulphurised olefins, mixed co-sulphurised fats and olefins, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, and sulphurised Diels-Alder adducts; phosphosulphurised hydrocarbons, such as the reaction product of phosphorus sulphide with turpentine or methyl oleate, phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, *i.e.*, dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite, metal thiocarbamates, such as zinc dioctyldithiocarbamate and barium heptylphenol diacid, such as zinc dicyclohexyl phosphorodithioate and the zinc salts of a phosphorodithioic acid; or mixtures thereof. The extreme pressure agents may be used alone or in combination.

Additionally the grease composition optionally includes friction modifiers including fatty amines, esters such as borated glycerol esters, fatty phosphites, fatty acid amides, fatty epoxides, borated fatty epoxides, alkoxylated fatty amines, borated alkoxylated fatty amines, metal salts of fatty acids, fatty imidazolines,

condensation products of carboxylic acids and polyalkylene-polyamines, amine salts of alkylphosphoric acids; viscosity modifiers including copolymers of styrene-butadiene rubbers, ethylene-propylene, polyisobutenes, hydrogenated styrene-isoprene polymers, hydrogenated isoprene polymers, polymethacrylate acid esters, polyacrylate acid esters, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins, polyalkylmethacrylates or esters of maleic anhydride-styrene copolymers; and dispersant viscosity modifiers (often referred to as a DVM) include functionalised polyolefins, for example, ethylene-propylene copolymers that have been functionalized with the reaction product of maleic anhydride and an amine, a polymethacrylate functionalised with an amine, or styrene-maleic anhydride copolymers reacted with an amine.

Other performance additives are optionally present in the grease composition, such as rust inhibitors including octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine; metal deactivators including derivatives of benzotriazoles, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles or 2-alkyldithiobenzothiazoles; foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides; and seal swell agents including Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil (FN 3200).

### Process

The invention further provides a process for preparing a grease composition comprising the steps of:

- (1) mixing an esterified polymer derived from monomers comprising (i) a vinyl aromatic monomer; (ii) an unsaturated dicarboxylic acid anhydride or derivatives thereof; and a solvent to form a solvated polymer;
- (2) reacting the solvated polymer of step (1) with at least two alcohols containing (i) at least about 6 carbon atoms and (ii) the other containing less than about 6 carbon atoms to form a solvated polymer containing an ester or derivatives



thereof; at a pressure from about 650 mm of Hg (about 86 kPa) to about 2000 mm of Hg (about 267 kPa); at a temperature from about 25°C to about 250°C preferably about 50°C to about 200°C, more preferably about 55°C to about 175°C and most preferably about 60°C to about 150°C; and for a period of time from about 1 minute to about 48 hours, preferably about 2 minutes to about 36 hours and most preferably about 3 minutes to about 30 hours;

(3) optionally, reacting the solvated polymer containing an ester or derivatives thereof an amine with primary functionality, secondary functionality or mixtures thereof to form an amidated polymer; at a pressure from about 650 mm of Hg (about 86 kPa) to about 2000 mm of Hg (about 267 kPa); at a temperature from about 50°C to about 250°C preferably about 60°C to about 200°C, more preferably about 65°C to about 175°C and most preferably about 70°C to about 150°C; and for a period of time from about 1 minute to about 48 hours, preferably about 2 minutes to about 36 hours and most preferably about 3 minutes to about 30 hours;

(4) adding the solvated polymer containing an ester or derivatives thereof of step (2) or the amidated polymer of step (3) to a thickening agent, an oil of lubricating viscosity or mixtures thereof; at a pressure from about 650 mm of Hg (about 86 kPa) to about 2000 mm of Hg (about 267 kPa); at a temperature from about 25°C to about 250°C preferably about 25°C to about 200°C, more preferably about 30°C to about 175°C and most preferably about 35°C to about 150°C; and for a period of time from about 1 minute to about 48 hours, preferably about 2 minutes to about 36 hours and most preferably about 3 minutes to about 30 hours; and

(5) optionally adding to the product of step (4) adding at least one other performance additive to form a grease composition.

The optional solvents include aliphatic solvents, aromatic solvents, alcohols, ethers, esters, an oil of lubricating viscosity or mixtures thereof. Examples of suitable the optional solvents include hexane, cyclohexane, heptane, mineral spirits, petroleum ether, benzene, toluene, xylene; iso-propanol, iso-butanol, 2-ethylhexanol, diethyl ether, methyl tert-butyl ether, ethyl acetate, iso-amyl acetate or mixtures thereof.

When the solvated polymer of step (1) is reacted with at least two alcohols, the alcohols are charged in a sufficient level to provide a product of step (2) with a

TAN of at least about 4. When present the process includes the addition of the methacrylate or acrylate monomer in step (1).

When present an esterification catalyst includes an acid, a base or mixtures thereof. Examples of suitable catalysts include methane sulphonic acid, mineral  
5 acids, tin salts, organo titanates, silica gel, cation-exchange resins or mixtures thereof. In one embodiment the catalyst is methane sulphonic acid or mixtures thereof.

When used as a solvent, the oil of lubricating viscosity may be the same or different to the oil of lubricating viscosity of the grease. Although the oil of  
10 lubricating viscosity may be used as a solvent, an aromatic solvent is preferred. In one embodiment the solvent is toluene or mixtures thereof. When present solvent, can be used alone or in combination.

#### Industrial Application

The grease composition of the present invention will be used for  
15 imparting at least one improved property including improved water repellence, improved water wash-off, improved thickening, increased longevity and decreased wear. In one embodiment the grease composition is used in an emulsified grease.

The following examples provide an illustration of the invention. It should  
20 however be noted that these examples are non exhaustive and not intended to limit the scope of the invention.

#### SPECIFIC EMBODIMENT

##### **Examples**

##### Example 1 and Reference Example R1

##### 25 Preparative Example 1

A four neck round bottom flask with a volume of about 5 litres, is charged with about 454g of a maleic anhydride-styrene copolymer and about 1000g of toluene solvent and stirred to form a mixture. The mixture is heated to about 120°C in a nitrogen atmosphere and a mixture of alcohols are added containing about 592g  
30 of Alfol C<sub>12</sub>-C<sub>18</sub> and about 198g of Alfol C<sub>8</sub>-C<sub>10</sub>. The mixture is stirred for about 30 minutes before the dropwise addition of a catalytic amount of methane sulphonic acid (about 23g) in about 200 cm<sup>3</sup> of toluene over a period of about 1 hour. The

reaction is held at about 120°C for about 24 hours before the addition of about 16.8g of butanol and the reaction is held for about another 3 hours followed by vacuum solvent stripping of toluene. The product is diluted to about 20 wt % in diluent oil before filtering. The final product has a total acid number of about 8-21 and a molecular weight of about 266,000.

#### Preparative Example 2

The product of Preparative Example 2 is the same as Preparative Example 1, except about 26.6g of N-(3-aminopropyl) morpholine is added immediately before vacuum solvent stripping of toluene.

#### Example 1

A grease formulation is prepared using a NLGI grade 2 grease containing lithium 12-hydroxy stearate and about 0.25g of the polymer prepared in Preparative Example 2.

#### Example 2

Example 2 is a lithium 12-hydroxystearate grease prepared in naphthenic oil. The grease is treated with the polymer prepared in Preparative Example 2 at about 0.6 wt % (on an oil free basis) of the grease composition.

#### Example 3

Example 3 is the same as Example 2, except the grease is treated with the polymer prepared in Preparative Example 1.

#### Example 4

Example 4 is a NLGI grade 2 lithium grease containing about 85 wt % of the grease composition (a) a 800 SUS paraffinic base oil containing unmilled lithium; (b) about 14.26 wt % of the grease composition a 800 SUS paraffinic base oil; and (c) about 0.6 wt % (on an oil free basis) the polymer prepared in Preparative Example 1.

#### Example 5

Example 5 is the same as Example 4, except the polymer prepared in Preparative Example 2 is used instead of the polymer prepared in Preparative Example 1.

#### Example 6

Example 6 is a grease composition containing 99.1 wt % of the composition of Example 2, except the grease is heated to about 54°C and about 0.74 wt % (on an oil free basis) the polymer prepared in Preparative Example 2 is added and milled.

#### 5 Example 7

Example 7 is the same as Example 6, except the polymer of Preparative Example 2 is added at about 0.31 wt% (on an oil free basis).

#### Example 8

10 Example 8 is the same as Example 6, except the grease composition is (a) a 800 SUS paraffinic base oil containing unmilled lithium 12-hydroxystearate; (b) about 14.26 wt % of the grease composition is a 800 SUS paraffinic base oil.

#### Example 9

Example 9 is the same as Example 8, except the polymer of Preparative Example 2 is added at about 0.31 wt% (on an oil free basis).

#### 15 Reference Example R1

Reference Example R1 is a grease formulation similar to Example 1, except the polymer of the invention is excluded.

#### Test 1

20 The ASTM D4049 test measures the resistance of grease to water spray. A pre-weighed stainless steel panel is evenly coated with about 8mm of grease. The panel is then reweighed. The coated stainless steel panel is then placed in a water spray for about 5 minutes. The water is preheated to about 38°C and held at constant temperature. The water pressure pump is held at about 276 kPa (equivalent to about 40 psi). The panel is removed from the spray and heated in an oven for about 1 hour  
25 at about 66°C. The panel is then removed from the oven, allowed to cool and is reweighed. The results obtained for the grease compositions are shown in Table 1 below.

Table 1: ASTM D4049 Results

Example	% Grease Removed by Water Spray
R1	60
1	31.9
2	16.2
3	20.2
4	21.6
5	18.6
6	25.7
7	35.5
8	47.6
9	61.9

The results indicate Examples 1 to 8 have better resistance to water spray than the reference example. Grease with better resistance to water spray have increased longevity and/or decreased wear.

5 Test 2

The ASTM D1264 test measures the water washout characteristics of greases. A tared bearing is packed with about 4g of grease and inserted into the apparatus described in ASTM D1264. A minimum of about 750 ml of distilled water preheated to about 79°C is added to the reservoir, but the water level is below the bearing. The water is re-circulated with a water pump and reheat to the about 79°C. When the water reaches about 79°C the water is sprayed at a rate of about 5 ml s<sup>-1</sup> over the bearing. The bearing is rotated at a speed of about 600 rpm for about 1 hour. The bearing is removed from the apparatus and dried for about 15 hours at about 77°C. The remaining grease is reweighed. The results obtained for the grease compositions are shown in Table 2 below.

Table 2: ASTM D1264 Results

Example	% Grease Removed by Water Washout
R1	10.9
1	1.9
2	4.1
3	2.5
4	3.6
5	3.4
6	5.51
7	5.37
8	5.13
9	5.51

Examples 1 to 9 have better water washout properties than the reference example. Grease with better water washout properties have increased longevity and/or decreased wear.

5 In summary the tests illustrate that the polymer of the invention provides grease compositions with improved water washout and spray-off properties. These enhanced properties further provide decreased wear and improved longevity of the grease.

10 While the invention has been explained, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.